WO 01/71394

SPECIFICATION

ANTIREFLECTION PRODUCT AND PRODUCINT METHOD THEREFOR

TECHNICAL FIELD

The present invention relates to an antireflection product having an optical thin film including pores which are penetrating one-dimensionally (hereinafter also called one-dimensionally penetrating pores). The optical thin film in the present invention is adapted for use in an antireflection film for a front glass of a display, a windshield glass of a vehicle, a window pane of a building, a mirror, an optical lens and the like, and has an excellent durability.

BACKGROUND TECHNOLOGY

A glass is employed in displays for a personal computer or a computer, but an ordinary glass surface reflects several percent of the incident light to cause reflections of a fluorescent light and a surrounding scene thereby resulting a drawback of hindering the visibility of the displayed content. Similar phenomena also become a problem in glass for buildings and furnishings such as a glass for a picture frame and a glass for a show window.

Also in a cover glass for a solar cell or a solar water heater, and in optical members such as eyeglasses and a camera, a low reflectance is desirable in order to fully exploit the performance thereof.

In a windshield glass for an automobile or a railroad vehicle, desired are a high transmittance and a low reflectance for reducing the reflection or glittering in an operation during nighttime to assist safe operation. A material having both a high transmittance and a low reflectance is required in wide fields, not only in glass but also in plastics. Also in case of under a relatively harsh environment such as a windshield glass for a vehicle, there are required not only a low reflectance but also a durability capable of maintaining such ability over a time.

Conventionally, in order to obtain a glass or plastics of a high transmittance by suppressing the surface reflection, an antireflection treatment utilizing optical interference has been utilized by providing the surface of the glass or plastics with a film having a low reflectance (for example a surface coating by a single-layered film of a low refractive index or by a multi-layered optical film formed by alternately laminating a layer of a low refractive index and a layer of a high refractive index).

For reducing the reflectance in a wide wavelength range in the visible region, the multi-layered optical film of the latter is desirable, but it is necessary in this method to laminate films of different compositions in two, three or more layers. Also in order to obtain a low refractive index by a single-layered film, it is necessary to select a material or a high durability that has a refractive index lower than that of glass or plastics and that is excellent in abrasion resistance, chemical resistance or moisture resistance. However, a material that can satisfy all these requirements has not been available.

For example, as a material of a lower refractive index than in the commonly utilized soda lime glass (refractive index 1.52), for example MgF_2 (refractive index 1.22) and Al_2F_3 (refractive index 1.36) are known, but such fluorides are inferior in the moisture resistance and the oxidation resistance to oxide materials such as SiO_2, and are not used much as the coating material on the glass surface requiring durability.

In addition to the inorganic films, there is also investigated a low-reflectance multi-layered film (Japanese Patent Application Laid-Open No. 5-254073) obtained by forming, on an undercoat layer of a cured film prepared by curing an acrylic copolymer

with a crosslinking material, a polymer film having a fluorine-containing alicyclic structure (Japanese Patent Application Laid-Open No. 2-019801). This multi-layered film has no problem in adhesion when the substrate is formed by plastics, but cannot obtain a sufficient adhesion strength when the substrate is a glass.

On the other hand, there has been a technology of forming a film such as of an oxide with satisfactory adhesion onto the surface of glass or plastics. For example, SiO_2 (having refractive index of 1.44 to 1.47 in a dense material) can be formed by a sputtering method or by a sol-gel method with satisfactory adhesion onto the aforementioned substrate.

However, the film formed by such method is a dense film, having a refractive index not much different from that of the substrate glass (for example soda lime glass having a refractive index of 1.52), and is therefore practically insufficient in the low reflectance. Therefore, it has been tried to reduce the refractive index of the film by introducing, into the film of SiO_2 or the like, pores sufficiently smaller than the wavelength of the light.

Some methods of obtaining a low refractive index film by introducing pores comparable with or smaller than the wavelength of the light into the

film, has been proposed. For example known is a method (J. Opt. Soc. Amer., 66, 515(1976)) of subjecting a borosilicate glass material to a Spinodal decomposition and executing an etching with a mixture of a solution of ammonium fluoride in hydrofluoric acid and a nitric acid solution to porosifying the vicinity of surface thereby forming a layer of a low refractive index, but the usable substrate in this case is limited to a borosilicate glass.

Also as another method, known is a method of preparing a ceramic slurry, containing fine powder of silica or alumina, then coating the slurry on the surface of glass or plastics by a immersion method or a doctor blade coating method, and heating, drying or sintering the coated slurry to form a porous inorganic film. However, an increase in the pore rate for obtaining a lower refractive index often leads to a drawback, contradictory in the performance, of a decrease in the strength of the film itself and a decrease in the adhesion strength between the film and the substrate.

An object of the present invention is to solve the drawbacks in the prior technologies and to provide an antireflection product that is low in refractive index, high in film strength and excellent in adhesiveness to the substrate.

The present invention also provides a producing method for an antireflection product, capable of producing the antireflection product without restriction on the substrate.

DISCLOSURE OF THE INVENTION

The present invention provides an antireflection product having on a substrate an optical thin film which is formed by removing one-dimensionally grown columnar phases from a composite film consisting of many one-dimensionally grown columnar phases and matrix phases surrounding the former, and in which are formed many pores continuing from one surface to the other of the film, surrounded by walls, and one-dimensionally penetrating, characterized in that the refractive index of the optical thin film is lower than that of the substrate and between that of the materials constituting the optical thin film and one.

The refractive index in the present invention means a refractive index at a wavelength of 550 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view illustrating a procedure for forming the optical thin film of the present invention.

DESCRIPTION OF SYMBOLS

1: substrate

2: columnar phase

3: matrix phase

4: composite film

5: optical thin film

6: amorphous precursor film

BEST MODE FOR CARRYING OUT THE INVENTION

The optical thin film in the present invention is an optical thin film having many one-dimensionally penetrating pores surrounded by walls continuing from one surface to the other of the film, and has a refractive index that is between a refractive index of the material (dense member) constituting the optical thin film and one, and that corresponds to a pore rate thereof.

With a pore rate R and a refractive index n of the matrix phase (dense member), and with the refractive index of the air being 1, the refractive index N of the optical thin film having the one-dimensionally penetrating pores can be approximately represented by $N = n \times (1 - R) + 1 \times R$.

In the present invention, for the purpose of providing an antireflective property, the refractive index of the optical thin film is selected smaller than the refractive index of the substrate.

The film thickness of the optical thin film is preferably from 60 to 200 nm. A film thickness less than 60 nm is difficult to obtain a sufficiently low reflectance, and tends to result in an insufficient film strength. Also a film thickness exceeding 200 nm is difficult to obtain a low reflectance over a wide wavelength region, and tends to cause a peeling of the film. For example at a film thickness of 50 nm, the low reflectance in the visible region is insufficient and the film strength is insufficient, and, at a film thickness of 250 nm, the reflection cannot be suppressed over a wide region and a partial peeling may occur in a drying step after the etching.

In the present invention, a ratio (d/r) of the average pore diameter (r) of the pore and the average thickness (d) of the wall is preferably from 0.1 to 0.3. A ratio less than 0.1 decreases the strength of the film, and a ratio exceeding 0.3 is difficult to obtain a sufficiently low reflectance.

The optical thin film of the present invention is formed by at least one selected from a group of oxides, carbides, nitrides, borides and fluorides, and is selected according to the purpose, but an oxide is most preferable in view of durability, strength, chemical stability and ease of formation.

The one-dimensionally penetrating pores preferably have an average pore diameter of from 1 to

500 nm. At a pore diameter less than 1 nm, the one-dimensionally extending phase tends to lack continuity, and is not eliminated after the etching to be described later and often remains in the matrix phase. When the phase to be removed remains, often generated are drawbacks such as a metallic reflection and a coloration.

Also at an average pore diameter exceeding 500 nm, large pores (having diameter of from about 500 to 1000 nm) often remain after the etching to cause a haze (film becoming turbid in milk-white color by the light scattering by the large pores). The average pore diameter is particularly preferably from 1 to 100 nm.

The present invention enables, by suitable selection of the material and the pore rate, to obtain a film having both a durability and a low refractive index, and can provide an antireflection product having only one layer of the optical thin film on the substrate.

For example, by forming the optical thin film with a material "being high in durability but not sufficiently low in refractive index", such as titania, silica, alumina, zirconia, silicon nitride, aluminum nitride, tin oxide, zinc oxide, tungsten oxide, nickel oxide or indium-tin oxide (ITO), both the durability and the low refractive index can be

satisfied by one layer only.

It is also possible to form a multi-layered film by combining the optical thin film of the present invention with another film. For example, the aforementioned optical thin film can be utilized as one layer in a multi-layered film such as a multi-layered antireflection film, a multi-layered heat ray reflection film, a multi-layered electroconductive film.

As a multi-layered antireflection film, for a wavelength λ of a light to be prevented from reflection, typical examples include 1) a two-layered antireflection film of a structure, from the substrate side, of high refractive index layer-low refractive index layer with optical thicknesses of $\lambda/2$-$\lambda/4$ (or $\lambda/4$-$\lambda/4$), 2) three-layered antireflection film of a structure, from the substrate side, of medium refractive index layer-high refractive index layer-low refractive index layer with optical thicknesses of $\lambda/4$-$\lambda/2$-$\lambda/4$, and 3) a four-layered antireflection film of a structure, from the substrate side, of low refractive index layer-medium refractive index layer-high refractive index layer-low refractive index layer with optical thicknesses of $\lambda/4$-$\lambda/2$-$\lambda/2$-$\lambda/4$. The optical thin film is suitable as the low refractive index layer for such multi-layered antireflection film.

Also known is a two-layered light absorbing antireflection member of a structure of substrate/light absorbing film/low refractive index film (Japanese Patent Application Laid-Open No. 9-156964 and Japanese Patent Application Laid-Open No. 10-96801). The optical thin film is also usable as the low refractive index film of such light absorbing antireflection member.

In the antireflection product of the present invention, a reflectance to an incident light from the film side of the optical thin film (reflectance by the film side surface excluding the reflection by a surface opposite to the film side, hereinafter also called a film surface reflectance) is preferably reduced by 40% or more (in particular 60% or more) in case of a 15° incident light, with respect to the reflectance the substrate without the optical thin film (blank). Also in a product bearing a multi-layered film including the optical thin film, in a measurement of a reflective spectrum to a 15° incident light from the film side of the optical thin film (reflective spectrum of the film side surface only, excluding the reflection by a surface opposite to the film side), the reflectance is preferably 1% or less in a wavelength region of from 400 to 700 nm. Also in case of an adhered glass in which a glass having an optical thin film is adhered with another

glass across an intermediate film, a film surface reflectance to a 60° incident light is preferably reduced by 40% or more, with respect to the reflectance in the case without the optical thin film (blank).

Also the optical thin film of the present invention, when employed in an outermost layer (outermost surface) of the antireflection product of the present invention, can exhibit another function by a suitable selection of the material. For example an optical thin film formed by silicon oxide can realize a contact angle to water of 5° or less (exhibiting a hydrophilicity), thereby providing an antifogging ability in addition to the low reflectance. Also an optical thin film formed by titanium oxide (particularly titanium oxide containing an anatase crystalline phase and/or a rutile crystalline phase) can exhibit a self-cleaning ability by a photocatalytic activity and a hydrophilicity.

Also a construction having the optical thin film formed by silicon oxide in an outermost layer (outermost surface) of the antireflection product of the present invention and having a titanium oxide layer (particularly titanium oxide layer containing an anatase crystalline phase and/or a rutile crystalline phase) immediately under the optical thin

film provides an antireflection product having an antifogging ability with durable hydrophilicity.

In the following, a producing method for the optical thin film will be explained.

In the present invention, a matrix phase is a material constituting the optical thin film and is a dense member. The optical thin film of the present invention is formed for example by a process of two stages. In a first stage, formed is a composite film constituted of many columnar phases grown one-dimensionally and matrix phases surrounding the former, and a second stage eliminates the columnar phases, grown one-dimensionally in the composite film, by an etching to leave the matrix phases only.

The method of forming the composite film in the first stage includes a method of directly forming the composite film constituted of one-dimensionally grown columnar phases and matrix phases surrounding the former by a physical film forming method (hereinafter also called a first forming method for the composite film), and a method of at first forming an amorphous precursor film on the substrate, and causing an eutectic reaction by a heat treatment thereby forming a composite film constituted of one-dimensionally grown columnar phases and matrix phases surrounding the former (hereinafter also called a second forming method for the composite film).

Fig. 1 is a schematic view illustrating a procedure of forming the optical thin film, in which a to d illustrate procedures of forming the optical thin film of the present invention, by the first forming method for the composite film: including a) a state (initial state) where a composite film 4, constituted of columnar phases 2 and matrix phases 3 by a physical film forming method on a substrate 1; b) a state (intermediate state) where the composite film 4 is similarly formed; c) a state where the formation of the composite film 4 is completed; and d) a state where an optical thin film 5 is formed by removing the one-dimensionally grown columnar phases 2 by a selective etching.

Also e to h illustrate procedures of forming the optical thin film of the present invention, by the second forming method for the composite film: including e) a state where an amorphous precursor film 6 containing a transition metal is formed on a substrate 1; f) a state where an eutectic structure is formed on the film surface by a heat treatment; g) a state where an interface of eutectic reaction is displaced by an oxygen diffusion from the surface to an interface between the film and the substrate to finally form an eutectic structure constituted of one-dimensionally grown columnar phases (crystals of transition metal oxide) 2 and matrix phases 3

surrounding the former thereby providing a composite film 4; and h) a state where an optical thin film 5 is formed by removing the one-dimensionally grown columnar phases 2 by a selective etching.

In the following, the "first stage" in the optical thin film formation will be described.

At first described is a case of utilizing the first forming method for the composite film.

In the first forming method for the composite film, examples of the physical film forming method for forming the composite film include a sputtering method, an evaporation method, a CVD method, a laser ablation method, and a molecular beam epitaxy method. Among these, particularly preferred is the sputtering method, as it easily provides a dense film, it is capable of providing a film having a high adhesiveness to the substrate and it is excellent in mass producibility and large-area film formation.

In the case of forming the composite film by the first forming method for the composite film, the materials for the columnar phases and the matrix phases may be in such a combination that the materials for the columnar phases and the matrix phases cause a phase separation at the film formation. In the present invention, as the columnar phases are utilized as pores after the etching while the matrix phases surrounding the columnar phases are utilized

as remaining phases, the material for the columnar phases is preferably a metal or an alloy that grows easily in a columnar shape, that is easily dissolved in an acid or an alkali and that is easily reduced with a little bonding energy with the material of the matrix phases.

Examples of the material for the columnar phases include, in consideration of practical ease of handling at the sputtering, at least one selected from the group of 3d transition metals (V, Cr, Mn, Ni, Fe, Co, Cu and Zn), alloys containing 3d transition metals, alkali earth metals (such as Mg) and alloys containing the alkali earth metals. In addition, Al, In, Sn and Pb are also usable.

Examples of the matrix phases, to be utilized as the remaining phases, include oxides such as silica, alumina, titania, zirconia, mullite, cordierite, spinel, zeolite and forsterite; carbides such as silicon carbide, titanium carbide, zirconium carbide and boron carbide (B_4C); borides such as titanium boride, zirconium boride, and boron carbide; nitrides such as silicon nitride, titanium nitride, and zirconium nitride; and fluorides such as magnesium fluoride and aluminum fluoride. Also the aforementioned materials may be contain a dopant of a small amount, within an extent of the permissible refractive index.

In the first forming method for the composite film, a mixing ratio of the materials for the columnar phases and the matrix phases and film forming conditions are controlled to form a fine structure in which the matrix phases surround the one-dimensionally grown columnar phases. For example in case of forming the composite film by the sputtering method, it is confirmed that the average diameter of the grown columnar phases changes by a volume ratio of the columnar phases and the matrix phases and by film forming conditions (for example by an Ar gas pressure and the substrate temperature at the sputtering).

As the diameter of the one-dimensionally penetrating pore approximately coincides with the diameter of the one-dimensionally grown columnar phase, the average pore diameter of the one-dimensionally penetrating pores in the optical thin film, finally obtained after the etching, can be changed by the mixing ratio of the materials for the columnar phases and the matrix phases and the film forming conditions (for example by the Ar gas pressure and the substrate temperature at the sputtering). It is confirmed, for example in a Co-SiO_2 system without heating of the substrate, Co in the film formed under an Ar gas pressure of 2 Pa has a particle diameter of 8 nm, while Co in the film

formed under an Ar gas pressure of 8 Pa has a particle diameter of about 40 nm.

In the following, there will be described an example of producing an antireflection product utilizing a sputtering method as the first forming method for the composite film.

The present invention provides a producing method for an antireflection product by sputtering a target constituted of a material for forming columnar phases and a material for forming matrix phases to form, on a substrate, a composite film constituted of many columnar phases grown one-dimensionally and matrix phases surrounding the former, and by removing the columnar phases to form an optical thin film containing many pores continuing from one surface to the other of the film, surrounded by walls formed by the matrix phases, and one-dimensionally penetrating, characterized in that the refractive index of the optical thin film is lower than that of the substrate and between that of the material constituting the optical thin film and one.

Examples of the target include 1) a target obtained by mixing and molding a powder of a material for forming the columnar phases and a powder of a material for forming the matrix phases, 2) a composite target prepared by placing, on a target of a material for forming the columnar phases, many

small pieces of about several millimeters of a material for forming the matrix phases, and 3) a composite target prepared by placing, on a target of a material for forming the matrix phases, many small pieces of about several millimeters of a material for forming the columnar phases.

In the present invention, it is preferable to use a target in which the material for forming the matrix phases is TiO_2, SiO_2, ZrO_2, Si_3N_4 or MgF_2, and to use a target in which the material for forming the columnar phases is Co.

In view of obtaining an optical thin film having a ratio (d/r) of the average pore diameter (r) of the pore and the average thickness (d) of the wall, of from 0.1 to 0.3, it is preferable to utilize a target constituted of the material for forming the columnar phases and the material for forming the matrix phases, in which the area, on the target surface, of the material for forming the columnar phases represents a proportion of from 0.55 to 0.75 with respect to the entire target surface. The proportion is represented by $v_p/(v_p + v_m)$ in which v_p is the area of the material for forming the columnar phases on the target surface and v_m is the area of the material for forming the matrix phases on the target surface. A proportion less than 0.55 is difficult to obtain one-dimensional columnar

structures, while a proportion exceeding 0.75 reduces the strength of the obtained film. The target is obtained 1) by mixing and molding both powders in such a manner that the powder of the material for forming the columnar phases represents a proportion of from 0.55 to 0.75 in a volume ratio with respect to the entire amount, or 2) by disposing, on a target constituted of the material for forming the columnar phases, small pieces of the material for forming the matrix phases in such a manner that $v_p/(v_p + v_m)$ becomes from 0.55 to 0.75.

In case of film formation of a $Co\text{-}TiO_2$ type composite film, a target with $v_p/(v_p + v_m)$ of 0.8 may have resulted in a destruction by contraction of the film in a drying step after the etching because of a low mechanical strength of the obtained film, and was liable to generate a haze by a film peeling. Also in case of a target with $v_p/(v_p + v_m)$ of 0.5, Co (colored portion) tended to remain in the film even after the etching.

In the following described is a case of utilizing the second forming method for the composite film.

In the second forming method for the composite film, examples of the method for forming the amorphous precursor film include physical film forming methods such as a sputtering method, an

evaporation method, a CVD method, a laser ablation method, and a molecular beam epitaxy method, solution methods such as a sol-gel method, a spray pyrolysis method and a coating method, and a plating method. Among these, particularly preferred is the sputtering method, as it easily provides a dense film, it is capable of providing a film having a high adhesiveness to the substrate and it is excellent in mass producibility and large-area film formation.

In the case of forming the amorphous precursor film by the sputtering method, employed is a target constituted of a material for forming the columnar phases and a material for forming the matrix phases. Such target is obtained by mixing a powder of the material for forming the columnar phases and a powder of the material for forming the matrix phases. Specific examples include a target in which the material for forming the columnar phases is Fe_3O_4, and a target in which the material for forming the matrix phases is TiO_2, SiO_2, ZrO_2, Si_3N_4 or MgF_2.

In case of forming an amorphous precursor film of Fe-Si-O type, a mixture of Fe_3O_4 powder and SiO_2 powder may be used as the target.

In the second forming method for the composite film, the combination of elements to be contained in the initially formed amorphous precursor film includes a transition metal element, another metal

element and oxygen. The transition metal element may be an element that can be separated, after the heat treatment, from another metal element contained in the film to constitute separate compound phases, and, in view of ease of handling at the heat treatment, examples include at least one selected from the group of 3d transition metal elements (V, Cr, Mn, Ni, Fe, Co, Cu, Zn etc.), alloys containing the 3d transition metal elements, and rare earth elements (Ce, Nd, Sm, Er etc.).

The metal element other than the transition metal element may be one that does not react with the transition metal element at the subsequent heat treatment. The metal element other than the transition metal element becomes the matrix phases surrounding the columnar phases (acicular crystals of the transition metal compound) at the heat treatment and becomes the component constituting the film having the one-dimensionally penetrating pores after the etching, and is therefore selected according to the purpose of use of the film. Examples of the metal element other than the transition metal element include Si, Al, Mg, Zr, Sn and In.

In case of forming the amorphous precursor film by the sputtering, the diameter of the columnar phases which one-dimensionally grows by the subsequent heat treatment changes by an Ar gas

pressure at the sputtering. For example, in case of a Fe-Si-O type film, hematite (Fe_2O_3) of a diameter of about 4 nm is deposited by a heat treatment at 600°C of a film formed under an Ar gas pressure of 2 Pa, while hematite (Fe_2O_3) of a diameter of about 20 nm is deposited by a similar heat treatment of a film formed under an Ar gas pressure of 8 Pa. As the diameter of the one-dimensionally penetrating pore approximately coincides with the diameter of the one-dimensionally grown columnar phase, the average pore diameter of the one-dimensionally penetrating pores in the optical thin film, finally obtained after the etching, can be changed by the film forming condition (Ar gas pressure at sputtering).

In the second forming method for the composite film, the amorphous precursor film containing the transition metal element, another metal element and oxygen is heat treated to cause an eutectic decomposition reaction in which a transition metal oxide and another metal oxide are separately deposited. It is important that the deposition of two phases from the amorphous phase takes place simultaneously and from the film surface. The process condition at heating may be a condition inducing an eutectic decomposition reaction. More specifically, there may be employed a temperature at which the eutectic decomposition reaction can be

induced and can proceed at a sufficient velocity. More specifically, a temperature of from 400 to 650°C is preferable.

For inducing the eutectic decomposition reaction, the valence number of the transition metal has to be changed. For this purpose there may be utilized two methods, namely a method of treating the amorphous precursor film in an oxidative atmosphere, and a method of treatment in a reductive atmosphere. In case of an eutectic reaction of an oxide, a uniform eutectic structure may not be formed by the treatment in the reductive atmosphere. In such case, a uniform eutectic structure can be formed by a heat treatment in an oxidative atmosphere.

In the second forming method for the composite film, in case of forming an amorphous film of Fe-Si-O type on the substrate, it is preferable, in view of obtaining one-dimensionally grown iron oxide crystals, to form the film by the sputtering method utilizing a target in which the material for forming the columnar phases is Fe_3O_4 (magnetite) and the material for forming the matrix phases is SiO_2 (silica).

In the following, the "second stage" in the optical thin film formation will be described.

In the second stage, from the composite film formed in the first stage, the columnar phases, grown one-dimensionally, only are selectively etched with

an acid or an alkali and removed. Examples of the acid to be used in the etching include sulfuric acid, hydrochloric acid, nitric acid, oxalic acid and acetic acid. For example, for removing metallic Co from a metallic Co/SiO_2 composite film formed by the first forming method of the composite film, the metallic Co alone can be completely removed by a treatment with a 0.1 mol/L aqueous solution of nitric acid for several minutes.

Also in case of a Fe-Si-O type composite film formed by the second forming method of the composite film, the one-dimensionally grown hematite is soluble in an aqueous solution of hydrochloric acid while SiO_2 is insoluble in such solution, so that a selective etching can be achieved by immersing the film in an about 6 mol/L aqueous solution of hydrochloric acid.

The substrate for forming the optical thin film of the present invention is not particularly restricted.

1) In case of utilizing the first forming method for the composite film, a substrate or a film of glass, ceramics (including sapphire (alumina single crystal) or the like), metals and plastics may be used.

2) In case of utilizing the second forming method for the composite film, a substrate or a film of

glass, ceramics (including sapphire (alumina single crystal) or the like), and heat-resistant metals (such as a stainless steel formed by Fe, Ni, Cr, V and the like or an antioxidative alloy such as hastelloy) may be used.

As the effects of the present invention can be exhibited particularly conspicuously, the substrate is preferably a transparent substrate (such as a glass substrate, a single crystal substrate or a film substrate), and particularly preferably a glass substrate. The substrate preferably has a refractive index of from 1.5 to 1.7.

The antireflection product of the present invention is advantageously employable in a front glass of a display (such as a CRT panel), an automotive window glass (such as a windshield glass for a vehicle), a window pane for a building, a glass for mechanical apparatus (such as a door glass for an industrial refrigerator), a mirror or an optical lens.

The optical thin film of the present invention has a relatively large pore rate, since the pores are continuous from the film surface to the interior of the film. The pores, being sufficiently smaller than the wavelength of light, do not scatter the light, and the film has a refractive index between the refractive index of a dense member and the refractive index of air (refractive index: 1.00).

Also as the one-dimensionally penetrating pores are surrounded by the continuous matrix phases, the optical thin film, for a same material and a same pore rate, in principle has a larger film strength in comparison with the conventional porous inorganic film and also shows a satisfactory adhesiveness to the substrate. The larger film strength is due to a fact, in contrast to the conventional porous inorganic film formed by loose bonding of ceramic particles for example by sintering, that the matrix surrounding the one-dimensionally penetrating pores in the film of the present invention is a completely continuous integrally-molded substance.

Also as to the adhesiveness to the substrate, a film of a particularly high adhesiveness can be obtained by forming the composite film of the first stage (including the amorphous precursor film by the second forming method) by a sputtering method or the like. Also the conventional porous inorganic film, when the pore rate of the film is increased for reducing the refractive index, tends to result in drawbacks contradictory in the characteristics such as a loss in the strength of the film itself and in the adhesion strength between the film and the substrate, but the optical thin film of the present invention can improve the film strength and the adhesiveness to the substrate while maintaining a low

refractive index, thus having a low refractive index and a high durability at the same time.

EXAMPLES

(Example 1)

The first forming method for the composite film was used to form, on a silica glass (quartz) substrate of a thickness of 1.2 mm, a thin film of two phases of metallic Co and TiO_2. At the sputtering, employed was a composite target, formed by disposing, on a metallic Co target of a diameter of ca. 15 cm, TiO_2 crystals (rutile type) of a 5 mm square. The metallic Co target had a proportion of 7/10 with respect to the entire area of the target surface.

After the vacuum chamber was evacuated to 5 x 10^{-4} Pa, Ar gas was introduced with a flow rate regulation to obtain a gas pressure of 2 Pa in the interior of the vacuum chamber, and a plasma was generated by a high frequency input of 600 W. The film forming rate was about 0.25 nm/sec, and the substrate was heated to about 200°C at the film formation. Thus formed Co-TiO_2 composite film of a thickness of 120 nm, when observed under a TEM (transmission electron microscope), showed Co crystal grains grown in columnar shape with an average grain diameter of about 8 nm, with a deposition of amorphous TiO_2 at the grain boundary.

As the second stage, the Co-TiO_2 composite film prepared by the above-described method was immersed in a 0.1 mol/L aqueous solution of nitric acid for 5 minutes for dissolving out the Co grains, whereby the Co grains were almost dissolved out and a transparent film remained. The average pore diameter was about 8 nm. The film after the removal of Co columnar layer from the Co-TiO_2 composite film, when observed under a SEM (scanning electron microscope), was found to be a uniform film without any particular contrast, except that particulate substances of a diameter of about several tens of nanometers were present thereon in some locations. Also in a photograph in the cross-sectional direction, a film having a structure in the vertical direction was found to remain in close adhesion with the substrate.

The pore rate of the thus formed optical thin film, estimated from the isothermal absorption-desorption characteristics of N_2 gas, was about 73%. The measurement was conducted in the following manner. A sample, bearing the aforementioned optical thin films (film thickness: 1 μm) on both surfaces of a quartz glass substrate of a thickness of 0.1 mm, was prepared, and was subjected to a measurement of isothermal absorption-desorption characteristics of nitrogen gas at the temperature of liquid nitrogen by an automatic specific surface area measuring

apparatus ("Autosorb-1", manufactured by Quanta Chrome Inc.), and the pore rate was determined from a pore volume obtained from the absorption amount and from the film thickness.

Also a reflective spectrum was measured by an ordinary reflective spectrometer, at a reflection angle of 15°, on the optical thin film bearing surface of the silica glass plate on which the aforementioned optical thin film was formed, and on a silica glass plate not having the film. At the measurement of reflective spectrum, the reflection of the film surface side (hereinafter called film surface reflection) alone was measured by making the glass surface, opposite to the film bearing surface, coarse with a sandpaper and coating a black paint thereon. The silica glass plate bearing the optical thin film showed a reflectance at 550 nm of about 0.28%, which was made lower in comparison with that (4.2%) of the blank glass plate (corresponding to a reflectance reducing effect of 93%). A refractive index estimated from a minimum reflectance around 550 nm was about 1.30, which was significantly made smaller than the refractive index (about 2.5) of a dense TiO_2 film. The refractive index (n_f) of the optical thin film was estimated by an equation $n_f = (n_s)^{1/2} \times [1 + (R_m)^{1/2}]^{1/2}/[1 - (R_m)^{1/2}]^{1/2}$ when $n_f > (n_s)^{1/2}$ or an equation $n_f = (n_s)^{1/2} \times [1 - (R_m)^{1/2}]^{1/2}/[1 +

$(R_m)^{1/2}]^{1/2}$ when $n_f \leq (n_s)^{1/2}$ (n_s being refractive index of the substrate and R_m being a minimum reflectance about 550 nm).

Table 1 shows the refractive index of substrate, the refractive index of matrix phases, the refractive index of optical thin film, the ratio (d/r) of the average pore diameter (r) and the average wall thickness (d), the pore rate (%), and the reflection reducing effect (%) measured at the reflection angle of 15°. Results are shown similarly in the following examples. However, in Examples 9, 10, 12 and 13, the antireflection ability was evaluated in a different manner.

The durability of the aforementioned optical thin film (TiO_2 film of a film thickness of 120 nm having one-dimensionally penetrating pores) was investigated by a Taber abrasion test, and no change was observed in the transmittance etc. after 100 revolutions. The Taber abrasion test was conducted with a commercially available Taber abrasion ring of CS10 type and a grinding paper of equivalent to the grinding paper #AA180 defined in JIS R6252, by abrading the film by 100 revolutions at 60 rpm under a load of 500 g. The Taber abrasion test in the following Examples was also conducted in the same manner.

(Example 2)

On a soda lime glass substrate of a thickness of 1.2 mm, a Co-SiO_2 composite film was formed in the following manner. At the sputtering, employed was a composite target, formed by disposing, on a metallic Co target of a diameter of ca. 15 cm, SiO_2 glass chips of a 0.5 mm square in such a manner that Co and SiO_2 glass had an area ratio of 70 : 30. The film formation was conducted under sputtering conditions approximately same as those in Example 1. The Co-SiO_2 composite film thus formed had an internal structure similar to that of the film obtained in Example 1, wherein the columnar phases of Co crystalline grains were surrounded by amorphous SiO_2 matrix phases, but the Co crystals in the present case had an average grain diameter of about 10 nm.

The sample of a film thickness of about 120 nm, prepared by the aforementioned method, was etched with an aqueous solution of nitric acid as in Example 1, whereby the Co columnar phases were mostly dissolved out and the SiO_2 matrix phases at the grain boundary remained. The average pore diameter was about 10 nm. It had a minimum reflectance of 0.07% in the visible region and could be used as an antireflection membrane. In the durability measurement of the optical thin film by the Taber abrasion test as in Example 1, no change was observed in the transmittance etc. after the test.

A contact angle, measured by dropping a drop of a purified water of a diameter of about 1 mm onto the surface of the obtained film, was about 5°. Also when the glass substrate, bearing the obtained SiO_2 film, was cooled to about 5°C by maintaining for 1 hour in a refrigerator, then taken out and blown with a human breath, the area bearing the film did not show a fog but the glass surface without the film was fogged and became opaque by deposition of fine water drops.

(Example 3)

On a sapphire (single crystalline alumina) substrate of a thickness of 5 mm, a TiO_2 film containing one-dimensionally penetrating pores was formed with a thickness of about 120 nm in a similar manner as in Example 1. The minimum reflectance in the visible region was 0.01 %, thus providing an extremely excellent antireflection ability.

In the durability measurement of the optical thin film by the Taber abrasion test as in Example 1, no change was observed in the transmittance etc. after the test.

(Example 4)

On a polyethylene film sheet of a thickness of 1.8 mm, an SiO_2 film containing one-dimensionally penetrating pores was formed with a thickness of about 120 nm in a similar manner as in Example 3.

The minimum reflectance in the visible region was 0.07 %, thus providing an extremely excellent antireflection ability.

(Example 5)

On a soda lime glass substrate of a thickness of 1.2 mm, a Co-ZrO_2 composite film was formed in the following manner. At the sputtering, employed was a composite target, formed by disposing, on a metallic Co target of a diameter of ca. 15 cm, ZrO_2 chips of a 0.5 mm square in such a manner that Co and ZrO_2 had an area ratio of 60 : 40. The film formation was conducted under sputtering conditions approximately same as those in Example 1. The Co-ZrO_2 composite film thus formed had an internal structure similar to that of the film obtained in Example 1, wherein the columnar phases of Co crystalline grains were surrounded by amorphous ZrO_2 matrix phases, but the Co crystals in the present case had an average grain diameter of about 7 nm.

The sample of a film thickness of about 120 nm, prepared by the aforementioned method, was subjected to an acid treatment as in Example 1, whereby the Co columnar phases were mostly dissolved out and the ZrO_2 matrix phases at the grain boundary remained. The average pore diameter was about 7 nm. In the durability measurement of the optical thin film by the Taber abrasion test as in Example 1, no change

was observed in the transmittance etc. after the test.

(Example 6)

On a soda lime glass substrate of a thickness of 1.2 mm, a Co-Si_3N_4 composite film was formed in the following manner. At the sputtering, employed was a composite target, formed by disposing, on a metallic Co target of a diameter of ca. 15 cm, Si_3N_4 chips of a 0.5 mm square in such a manner that Co and Si_3N_4 had an area ratio of 60 : 40. The film formation was conducted under sputtering conditions approximately same as those in Example 1.

The Co-Si_3N_4 composite film thus formed had an internal structure similar to that of the film obtained in Example 1, wherein the columnar phases of Co crystalline grains were surrounded by amorphous Si_3N_4 matrix phases, but the Co crystals in the present case had an average grain diameter of about 6 nm.

The sample of a film thickness of about 120 nm, prepared by the aforementioned method, was immersed in an aqueous solution of nitric acid to dissolve out Co grains. As in Example 1, the Co columnar phases were mostly dissolved out and the Si_3N_4 matrix phases at the grain boundary remained. The average pore diameter was about 6 nm. In the durability measurement of the optical thin film by the Taber abrasion test as in Example 1, no change was observed

in the transmittance etc. after the test.

(Example 7)

On a soda lime glass substrate of a thickness of 1.2 mm, a Co-MgF_2 composite film was formed in the following manner. At the sputtering, employed was a composite target, formed by disposing, on a metallic Co target of a diameter of ca. 15 cm, MgF_2 ceramic chips of a 1 cm square, and the amount of MgF_2 chips was so regulated that Co and MgF_2 had an area ratio of 70 : 30.

The film formation was conducted under another sputtering conditions approximately same as those in Example 1. The Co-MgF_2 composite film thus formed had an internal structure similar to that of the film obtained in Example 1, wherein the columnar phases of Co crystalline grains were surrounded by amorphous MgF_2 matrix phases, but the Co crystals in the present case had an average grain diameter of about 12 nm.

The sample of a film thickness of about 120 nm, prepared by the aforementioned method, was immersed in a 0.1 mol/L aqueous solution of nitric acid for 5 minutes to dissolve out Co grains. As in Example 1, the Co columnar phases were mostly dissolved out and the MgF_2 matrix phases at the grain boundary remained. The average pore diameter was about 12 nm. In the durability measurement of the optical thin film by

the Taber abrasion test as in Example 1, no change was observed in the transmittance etc. after the test.

(Example 8)

On a heat resistant glass substrate (Corning #7059) of a thickness of 1.0 mm, a ternary Fe-Si-O amorphous precursor film was formed by a sputtering method. At the sputtering, a sintered mixture of Fe_3O_4 powder and SiO_2 powder in a volume ratio of 70% and 30% (namely $v_p(v_p + v_m) = 7/10$) was used as a target. After the vacuum chamber was evacuated to 5×10^{-4} Pa, argon gas was introduced with a flow rate regulation to obtain a gas pressure of 2 Pa in the interior of the vacuum chamber, and a plasma was generated by a high frequency input of 4.4 W/cm^2. The film forming rate was about 0.2 nm/sec.

Thus formed amorphous precursor film, in an observation under a SEM had a cross-sectional structure having an amorphous film of a thickness of about 120 nm on the glass substrate. The amorphous film was formed very densely, without defects such as a crack or a pore. Subsequently, the amorphous film was subjected to a heat treatment at 600°C for 2 hours in the air. In an observation under a TEM of the film after the heat treatment, one-dimensionally grown acicular hematite crystals (Fe_2O_3) and silica crystals (SiO_2) surrounding the former constituted an eutectic structure. The hematite crystals grew

perpendicularly to the film surface from the film surface to the interface with the substrate, and had a diameter of about 4 nm.

Finally, the film subjected to heat treatment above was immersed, together with the substrate, in an about 6 mol/L aqueous solution of hydrochloric acid at the room temperature for 48 hours to remove hematite only. In a TEM observation of the fine structure of the film cross section, penetrating pores of a diameter of 4 nm, substantially same as that of hematite prior to the acid treatment, were present in the remaining SiO_2 film. In the durability measurement of the optical thin film by the Taber abrasion test as in Example 1, no change was observed in the transmittance etc. after the test.

(Example 9)

On a soda lime glass substrate of a thickness of 1.2 mm, a three-layered film including SnO_2/SiO_2 (dense)/SiO_2 (containing one-dimensionally penetrating pores) from the substrate side was prepared in the following manner. After the vacuum chamber was evacuated to 5×10^{-4} Pa, oxygen gas was introduced under a flow rate regulation to obtain a pressure of 0.4 Pa, and a DC sputtering power of 330W was supplied to a Sn target of a diameter of about 15 cm to form a SnO_2 film of 14 nm. Then the substrate was moved above a silicon target of a diameter of

about 15 cm, and a DC sputtering power of 330 W, superposed with a positive pulse of 40 kHz, was supplied to the silicon target to form a SiO_2 (dense) film of 113 nm. Thereafter, a film formation was executed in the same manner as in Example 2 to form a SiO_2 film having one-dimensionally penetrating pores with a thickness of 123 nm.

The glass surface, opposite to the film forming surface, was made unsmooth with a sandpaper and coated with a black paint, and then a reflective spectrum on the film forming surface (hereinafter called film-forming surface reflective spectrum) was measured. The wavelength region in which the reflectance was 1% or less extended from 390 to 720 nm, and the optical multi-layered film thus had an extremely wide antireflection wavelength range.

(Example 10)

On a soda lime glass substrate of a thickness of 1.2 mm, a two-layered film including SnO_2/TiO_2 (containing one-dimensionally penetrating pores) from the substrate side was prepared in the following manner. After the vacuum chamber was evacuated to 5 x 10^{-4} Pa, oxygen gas was introduced under a flow rate regulation to obtain a pressure of 0.4 Pa, and a DC sputtering power of 330W was supplied to a Sn target of a diameter of about 15 cm to form a SnO_2 film of 7.5 nm. Thereafter, a film formation was executed in

the same manner as in Example 1 to form a TiO_2 film having one-dimensionally penetrating pores with a thickness of 109 nm.

In a measurement of film-forming surface reflective spectrum, the wavelength region in which the reflectance was 1% or less extended from 410 to 700 nm, and the optical multi-layered film thus had an extremely wide antireflection wavelength range.

(Example 11)

A Co-TiO_2 composite film was prepared in the same manner as in Example 1 except that the film thickness was changed to 140 nm, and was subjected to an etching. The obtained film had an average pore diameter of about 8 nm.

The glass substrate bearing the obtained TiO_2 film was placed in an electric furnace and heated at 600°C for 2 hours in the air, whereby the film thickness decreased by about 15% (namely the film thickness being about 120 nm), and the film was identified, in an X-ray diffractometry, to contain crystals of two types of anatase and rutile. The film had a refractive index of 1.3 and a minimum reflectance on the film surface of 0.28 %.

In the glass substrate with the TiO_2 film after the heating, the film surface was coated with oleic acid and subjected to a measurement of contact angle water, which was found as about 85°. Subsequently,

when the film of the glass substrate with the TiO_2 film was irradiated with a light (ultraviolet light) of 350 nm by a black light with an intensity of about 4 mW/cm^2. The contact angle of water was lowered to 15° after 240 hours, indicating that the hydrophilicity was restored by decomposition of oleic acid.

(Example 12)

On a soda lime glass substrate, a TiO_2 film of a thickness of 120 nm, containing anatase crystalline phases, was formed by a sol-gel method. Thereafter, a film formation was executed in the same manner as in Example 2 to form a SiO_2 film except that the film thickness was changed to 100 nm. In a peripheral portion of the substrate, a mask was so formed as not to form TiO_2 film nor SiO_2 film.

In a measurement of film-forming surface reflective spectrum, the wavelength region in which the reflectance was 1% or less extended from 410 to 700 nm, and the optical multi-layered film thus had an extremely wide antireflection wavelength range.

A contact angle, measured by dropping a drop of a purified water of a diameter of about 1 mm onto the surface of the obtained film, was about 5°. Also when the glass substrate, bearing the obtained SiO_2 film, was cooled to about 5°C by maintaining for 1 hour in a refrigerator, then taken out and blown with

a human breath, the area bearing the film did not show a fog but the glass surface without the film was fogged and became opaque by deposition of fine water drops.

The contact angle of water, measured again on the glass substrate bearing the obtained film after standing indoors for 3 months, was about 20°, indicating a loss in the hydrophilicity. When the film of the glass substrate with the TiO_2 film having lowered hydrophilicity was irradiated with a light (ultraviolet light) of 350 nm by a black light with an intensity of 4 mW/cm^2, the contact angle of water was lowered to 7° after 120 hours, indicating that the hydrophilicity was restored.

(Example 13)

On a soda lime glass substrate of a thickness of 2 mm for an automotive front glass, a SiO_2 film (having one-dimensionally penetrating pores) was prepared in the following manner. After the vacuum chamber was evacuated to 5×10^{-4} Pa, Ar gas was introduced with a flow rate regulation to obtain a gas pressure of 1 Pa, and a sputtering power of 40 kW was supplied to a Co-SiO_2 target of a length of 2.5 m to form a Co-SiO_2 film of a thickness of 134.5 nm. The obtained film was immersed in a 0.1 mol/L aqueous solution of nitric acid for 5 minutes for dissolving out the Co grains, whereby the Co grains were almost

dissolved out and a transparent SiO_2 film remained.

The glass substrate having thus obtained SiO_2 film and a glass substrate (2 mm thick) of a same shape without the film were adjoined across an intermediate film (polyvinylbutyral) in such a manner that the surface not bearing the SiO_2 film was in contact with the intermediate layer to obtain an adjoined glass for the automotive front glass.

The surface without the SiO_2 film of the adjoined glass for the automotive front glass was made unsmooth with a sandblast and coated with a black paint, and then a film surface reflection on the SiO_2 film forming surface was measured. When a light of a wavelength of 550 nm was made to enter the glass surface with an incident angle of 60°, the reflectance was about 8.2%, corresponding to a reflection reducing effect of 45%, in comparison with the value (about 15%) when the film was absent.

(Example 14)

In order to evaluate the adhesiveness of the film to the substrate, the samples of Examples 1 to 13 were subjected to a cellophane adhesive tape peeling test, according to a grid-tape method (JIS K5400). As a result, no practically unacceptable peeling was observed in any of the samples.

(Comparative Example 1)

On a silica glass substrate of a thickness of

1.2 mm, a solution of titanium isopropoxide dissolved at a concentration of 0.5 mol/L in propanol was coated and was heated to about 450°C to form a porous TiO_2 film of a thickness of 120 nm. In a measurement of durability by the Taber abrasion test as in Example 1, the film was partially peeled off at 100 revolutions whereby the transparency was deteriorated.

(Comparative Example 2)

On a heat resistant glass substrate (Corning #7059) of a thickness of 1.0 mm, a ternary Fe-Si-O amorphous precursor film was formed by a sputtering method. At the sputtering, a sintered mixture of FeO powder and SiO_2 powder in a volume ratio of 70% and 30% was used as a target. After the vacuum chamber was evacuated to 5×10^{-4} Pa, argon gas was introduced with a flow rate regulation to obtain a gas pressure of 2 Pa in the interior of the vacuum chamber, and a plasma was generated by a high frequency input of 4.4 W/cm^2. The film forming rate was about 0.2 nm/sec.

Thus formed amorphous precursor film, in an observation under a SEM, had a cross-sectional structure having an amorphous film of a thickness of about 120 nm on the glass substrate. The amorphous film was formed very densely, without defects such as a crack or a pore. Subsequently, the amorphous film was subjected to a heat treatment at 600°C for 2 hours in the air. In an observation under a TEM of

the film after the heat treatment, there was obtained a structure in which granular hematites crystals (Fe_2O_3) of a diameter of several nanometers were dispersed in a silica (SiO_2) matrix, and a one-dimensional eutectic structure could not be obtained.

Table 1

example	refractive index of substrate	refractive index of matrix phases	refractive index of optical thin film	d/r	pore rate (%)	reflectance of substrate (%)	film surface reflectance (%)	reflection reducing effect (%)
1	1.52	2.5	1.30	0.14	73	4.2	0.28	93
2	1.52	1.4	1.20	0.18	65	4.2	0.07	98
3	1.65	2.5	1.30	0.15	74	6.7	0.01	100
4	1.60	2.5	1.30	0.20	58	5.5	0.07	99
5	1.52	2.2	1.30	0.16	70	4.2	0.28	93
6	1.52	2.1	1.34	0.22	65	4.2	0.69	84
7	1.52	1.38	1.12	0.21	68	4.2	0.92	78
8	1.52	1.4	1.12	0.15	75	4.2	0.92	78
9	1.52	1.4	1.20	0.18	68	4.2	-	-
10	1.52	2.5	1.30	0.14	74	4.2	-	-
11	1.52	2.5	1.30	0.14	73	4.2	0.28	93
12	1.52	1.4	1.20	0.18	65	4.2	-	-
13	1.52	1.4	1.20	0.18	65	4.2	-	-

Industrial applicability

The optical thin film of the present invention includes many one-dimensionally penetrating pores, continuous from one surface to the other of the film and surrounded by walls, and has a low refractive index, a high film strength and an excellent adhesiveness to the substrate.

The present invention enables to provide an optical thin film of various compositions, applicable to various substrates, and a substrate equipped with the optical thin film.

Also the pores contained in the optical thin film of the present invention have substantially aligned diameters of about 1 to 500 nm, and huge pores of tens of micrometers are not present. Therefore, fine particles floating in the air, such as cigarette tar and dusts, cannot fit into the pores and can be easily removed by a simple washing.

CLAIMS

1. An antireflection product having on a substrate an optical thin film which is formed by removing one-dimensionally grown columnar phases from a composite film consisting of many one-dimensionally grown columnar phases and matrix phases surrounding the former, and in which are formed many pores continuing from one surface to the other of the film, surrounded by walls, and one-dimensionally penetrating, characterized in that the refractive index of the optical thin film is lower than that of the substrate and between that of the material constituting the optical thin film and one.

2. The antireflection product according to claim 1, wherein the optical thin film is constituted of silicon oxide or titanium oxide.

3. The antireflection product according to claim 1, wherein the optical thin film is constituted of titanium oxide containing an anatase crystalline phase and/or a rutile crystalline phase.

4. The antireflection product according to claim 1, comprising the optical thin film constituted of silicon oxide at an outermost layer and a titanium oxide layer containing an anatase crystalline phase

and/or a rutile crystalline phase directly under the optical thin film.

5. The antireflection product according to claim 1, wherein the optical thin film has a thickness of from 60 to 200 nm.

6. The antireflection product according to claim 1, wherein a ratio (d/r) of an average pore diameter (r) of the pores and an average thickness (d) of the wall is within a range of from 0.1 to 0.3.

7. A producing method for an antireflection product by sputtering a target constituted of a material for forming columnar phases and a material for forming matrix phases to form, on a substrate, a composite film constituted of many columnar phases grown one-dimensionally and matrix phases surrounding the former, and by removing the columnar phases to form an optical thin film containing many pores continuing from one surface to the other of the film, surrounded by walls formed by the matrix phases, and one-dimensionally penetrating, characterized in that the refractive index of the optical thin film is lower than that of the substrate and between that of the material constituting the optical thin film and one.

8. The producing method for the antireflection product according to claim 7, wherein the target has an area, on the target surface, of the material for forming the columnar phases representing a proportion of from 0.55 to 0.75 with respect to the entire target surface.

9. The producing method for the antireflection product according to claim 7, wherein, in the target, the material for forming the matrix phases is TiO_2, SiO_2, ZrO_2, Si_3N_4 or MgF_2.

10. The producing method for the antireflection product according to claim 7, wherein, in the target, the material for forming the columnar phases is Co or Fe_3O_4.